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16. ABSTRACT The methods of sampling ambient air for organic compounds for subsequent analysis are discussed. The following methods of sample collection are presented and the advantages and disadvantages of each is given: concentration of component of interest on to solid sorbents, into liquid sorbents or on to filter-sorbent combinations; cryogenic concentration; derivatization of the component of interest; integrated sampling into containers such as canisters and bags; and direct analysis. Sampling problems of breakthrough of component of interest, formation of artifacts during sampling and interferences from water collected from air during sampling are also discussed. The relative advantages of integrated sampling into containers versus concentrating on to sorbents and/or filters are presented.		
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1.0 INTRODUCTION

Ambient air can contain a large number of organic compounds at concentrations that make them of concern as air pollutants. As a general rule, organic compounds are present in ambient air in very low concentrations and this complicates the process of obtaining a sample for analysis. The low, but extremely important, levels of organic compounds in the ambient air generally require concentration from a rather large volume of air and this requirement exacerbates the problems of separation of components of interest, detection limit and sample contamination. There are a few techniques that allow the direct analysis of organic compounds which do not require concentration but they have not been applied widely and will not be dealt with in this paper.

Vapor pressure and polarity are the two most important properties governing the success of sampling organic compounds from ambient air. For organic compounds with medium to high vapor pressures, components of interest are usually concentrated from large volumes of air using a solid sorbent material of some sort. Low vapor pressure components are normally associated with particles and filtration of large volumes of air to collect the particles is the usual means of sample collection. In both cases analysis requires the separation of the sample from the matrix with further separation into individual components for analysis. Highly polar organic compounds are very difficult to sample properly. There is a strong tendency for these materials to adhere to the sampling media and sampling media containers. Separation of the sample from its matrix and separation into individual components are quite difficult and no really satisfactory method for sampling polar organic compounds is available at present.

Although sample analysis will not be discussed in this paper, the method of analysis needs to be kept in mind in the selection of sampling methodology. All methods of analysis require a preliminary separation in order to isolate the organic compound, or compounds, of interest. The limit of detection of the analytical method frequently governs how much sample is required and the ever present problem of interfering substances would be best dealt with, if possible, at the sampling stage by excluding the interfering substance.

2.0 VOLATILITY

It is useful to categorize the target organic compounds by their volatility and the designations "Volatile", "Semivolatile" and "Nonvolatile" have been suggested as three convenient categories for organic compounds in ambient air (1). The vapor pressure ranges suggested are:

	<u>Vapor Pressure, kPa</u>
Volatile	$>10^{-2}$
Semivolatile	10^{-2} to 10^{-8}
Nonvolatile	$<10^{-8}$

The discussion that follows will be organized along these categories and sampling methodology appropriate for each category will be presented.

3.0 VOLATILE ORGANIC COMPOUNDS

3.1 General Description of Methodology

Volatile organic chemicals have probably received more attention than any other group of organic chemicals present in ambient air. Important aromatic hydrocarbons, halogenated hydrocarbons, aldehydes and ketones are members of this category. The most widely used procedure for sampling ambient air for these compounds is to pass large volumes of air, typically two to 100 L, through a solid sorbent material on to which the component of interest is adsorbed. Unfortunately, solid sorbents are not compound specific and unwanted

compounds, as well as the target compounds, are collected and must be separated. Another concentration procedure which is undergoing a rebirth and rapidly gaining favor is the cryogenic condensation of volatile organics from air. Modern automation techniques, sensitive gas chromatography detectors and the availability of rugged inert sampling containers have made this long used method of collecting air samples quite attractive and several recent monitoring studies successfully employed cryogenic condensation for collecting volatile organics. For analysis the condensate from cryogenic sampling is separated by gas chromatography and a determination made by common detectors such as flame ionization detectors, electron capture detectors and mass spectrometric detectors.

3.2 Sorbent Sampling

Sampling with solid sorbents is commonly employed to obtain volatile organics from the atmosphere. Solid sorbent media can be divided into three categories, namely, organic polymeric sorbents, inorganic sorbents and carbon sorbents. Organic polymeric sorbents include materials such as Tenax and Amberlite XAD resins. These materials have the important feature that water is not collected in the sampling process, thus large volumes of air can be sampled. A major disadvantage is the inability of the polymeric sorbents to capture highly volatile organics (e.g., vinyl chloride) as well as certain polar materials (e.g., low molecular weight alcohols and ketones).

Inorganic sorbents include silica gel, alumina, Florisil, and molecular sieves. These sorbents are considerably more polar than the organic polymeric sorbents, thus permitting the efficient collection of polar organics. Unfortunately, water is also efficiently captured causing a rapid deactivation of the sorbent. For this reason inorganic sorbents are not often used for sampling volatile organics.

Carbon sorbents are relatively nonpolar compared to the inorganic sorbents and water is less of a problem, although the problem may still prevent analysis in some cases. Carbon sorbents exhibit much stronger adsorption properties than organic polymeric sorbents which allows for the efficient collection of volatile organics such as vinyl chloride. The strong adsorption of organics on carbon sorbents is a disadvantage because the removal of most of the collected chemicals requires displacement with a solvent and, as discussed below, this is not the isolation method of choice.

In considering the sorbent material for sampling for volatile organics one must consider both the capture process and the compound recovery process. One of two processes is used, thermal desorption and solvent extraction. Thermal desorption is most useful for compounds having boiling points less than 300 C whereas solvent extraction is most useful for compounds boiling above 150 C and is used extensively for semivolatile organics.

Tenax is the sorbent that has been most widely used for sampling volatile organics with subsequent thermal desorption and it is discussed in more detail later. Graphitized molecular sieves, such as Sphero carb and Amborsorb XE-340, can also be thermally desorbed. However, rather high desorption temperatures are required, making recovery of higher boiling volatile organics difficult and exacerbating decomposition problems. Thermal desorption is an attractive approach in many cases since the entire sample is introduced into the analytical system whereas in solvent extraction only a small portion (e.g., <1 to 10%) can be introduced. The use of the entire sample in thermal desorption permits collecting smaller air volumes in order to obtain sufficient sample for analysis. In addition, the thermal desorption process is more easily automated and does not require disassembly of the sampling cartridge prior to analysis. Solvent extraction offers the advantage that the

concentration of analyte introduced into the analytical system can be optimized and also allows replicate analyses of a sample, features not available in the thermal desorption process. On balance, however, the thermal desorption procedure is the preferred means for isolating a sample from its matrix for analysis.

Unfortunately sorbent sampling is fraught with problems. Contamination and interferences may be particularly troublesome. As mentioned previously, some popular solid sorbents have low capacities for volatile compounds and the resulting breakthrough of target compounds before the completion of sampling leads to erroneous determinations of atmospheric concentrations (2). Finally, unknown reactions can occur during sampling and, perhaps, during analysis (3-6). These reactions can lead to the incorrect determinations of compounds not present and prevent the accurate determination of compounds actually present in the air sampled. These potential problems require that sorbent sampling be planned and executed with great care.

3.3 Tenax Sampling

Because of its very widespread use in sampling for ambient organics, Tenax will be discussed separately. Tenax, a polymeric solid sorbent originally developed as a support for gas chromatography, is the most widely used solid sorbent for ambient air sampling (7-9). Tenax has the advantage of high thermal stability, which permits the thermal desorption of collected volatile materials. Tenax also has the advantage of a low affinity for water which means that little water from the atmosphere is collected to complicate sample isolation and analysis. Sampling with Tenax, thermal desorption, gas chromatographic separation and sample analysis with mass spectrometry has been the most widely used system for obtaining the concentrations of volatile organics in ambient air. Pellizzari and co-workers have developed and utilized

this system for the determination of volatile organics in the ambient air in a number of important studies (10).

Recent research has shown that quantitative interpretation of data from the collection of ambient organics using solid sorbents is complicated to a greater extent than previously believed. Walling (11,12) has discussed the problems associated with exceeding the capacity of adsorbent, inadequate blank correction and unwanted reactions occurring during the sampling and analysis process using Tenax sorbent sampling as his model. He has proposed a distributed air volume approach as a powerful quality control technique to help determine if complications which would invalidate the sample occurred during sampling. In the distributed air volume approach to air sampling, several (generally four) samples are obtained simultaneously from the same parcel of air with the important stipulation that a wide range of air volumes be sampled by using different air sampling flow rates for the same starting and stopping times. On completion of the sampling and analysis, the concentration of each target compound in each sample is compared across all samples taken during the sampling period. The results are sorted into two groups, one in which the concentrations of a target compound do not vary across all samples beyond expected laboratory variation and one group in which variation in concentrations of a target compound does exceed pre-established laboratory analytical variation. Constancy in concentrations across a set of samples for a target compound is presumptive evidence that the average of the values is a valid estimate of the concentration of the target compound in the ambient air at the time of the sampling. Sets of concentrations which exceed normal variation are not accepted as providing a valid estimate of air concentration and are investigated to determine if a cause for the problem can be found.

3.4 Canister Collection

The condensation of volatile organics from air into a cryogenic trap, particularly when combined with whole air sampling using appropriate containers, is an attractive alternative to sorbent sampling. Advantages of this technique are that a wide range of organics can be collected and determined, contamination problems are greatly reduced and consistent recoveries are generally obtained. An important limitation is the condensation of large amounts of moisture with the sample unless steps are taken to avoid the problem. As discussed below, this problem has been partially overcome.

A system of collection of whole air samples in stainless steel canisters whose interior walls have been specially electro-polished to prevent decomposition of the collected organics, cryogenic concentration of an aliquot and gas chromatography with detection by electron capture or flame ionization has been developed by McClenny (13) and applied to monitoring studies. The cryogenic condensation of sample and its separation and analysis have been automated (14). The problem of water corrupting the analysis has been dealt with by incorporating a drying step prior to chromatography. This is accomplished by passing the air sample through Nafion tubing before the cryogenic condensation. Nafion tubing has the valuable property of permitting water vapor in a mixture of gases passing through it to permeate through its walls while retaining most of the compounds of interest as air pollutants. This appears to be a phenomenon dependent upon polarity because other small polar molecules such as low molecular weight alcohols, aldehydes and ketones, will also permeate to some extent through the Nafion tubing walls. For this reason the system is restricted to the determination of relatively non-polar organics. Notwithstanding this restriction, the system can be used effectively to

monitor for important pollutants such as halogenated hydrocarbons and volatile aromatic hydrocarbons.

Sampling using canisters can be accomplished either by evacuating the container in advance and then allowing sample to enter the container or pressurizing a canister with sample air using pumps with inert interior surfaces. The latter approach is preferred when integrated samples over a relatively long, i.e. 12 hours, time period is desired.

3.5 Tenax, Canister Comparison

Side-by-side comparisons of samplers based on canisters and on Tenax have become a major effort in continuing the methods development for volatile organics. A comparison study in an unoccupied residence (15) proved to be a good example of the essential equivalency of the two sampling approaches in the absence of factors sometimes associated with ambient air sample collection, e.g., variations in temperature, water vapor content and the presence of high levels of ozone. Side-by-side comparisons in ambient air have been carried out but the analytical results have not yet been consolidated and interpreted to provide definitive conclusions. Ambient comparisons in EPA's Toxic Air Monitoring System (TAMS) are a continuing effort to show the degree of equivalency between the two sampling techniques.

4.0 SEMIVOLATILE ORGANIC COMPOUNDS

4.1 General Description of Methodology

Although semivolatile organic air pollutants have not received the broad interest as have volatile organics, there are some very important members of the class which have received considerable attention. Important class members are polynuclear aromatic hydrocarbons with four or less fused rings and their nitro derivatives, chlorobenzenes, chlorotoluenes, polychlorobiphenyls,

organochlorine and organophosphate pesticides and the various chloro-p-dibenzodioxins. As is the case with volatile organics, the concentrations of semivolatile organics in the ambient air are so low that concentrating the target compounds from a large air volume is required. A large volume of ambient air is passed through an appropriate solid sorbent, or filter-sorbent combination, to collect the compounds of interest. Solvent extraction is the universal method for isolating the organics from the sampling matrix and the analytical determination is made using gas chromatography with an appropriate detector.

The most popular sorbent for capturing semivolatile organics is polyurethane foam. This material efficiently collects many semivolatile organics from air and has the advantage of low resistance to air flow, thus permitting sampling of rather large volumes of air to obtain sufficient sample for analysis. Granular solid sorbents, such as Amberlite XAD-2, Chromosorb 102, Poropak R, Florisil and silica gel have also been used but they all have a much higher resistance to air flow and, for this reason, are not as widely used as is polyurethane foam.

A practical, field usable sampler incorporating polyurethane foam or granular sorbents has been developed by modifying the well known High Volume sampler used for collecting ambient particulate matter (16-18). In this modification, a cylinder of polyurethane foam or granular sorbent is inserted behind a glass or quartz fiber filter and the air flow rate reduced somewhat. Generally about 300 m³ of air is sampled as opposed to approximately 2000 m³ when the High Volume sampler is used in its normal configuration. Sampling periods up to 24 hours can be used and the semivolatile compounds of interest are isolated by extracting both the filter and the vapor trap with an appropriate solvent. A number of monitoring studies have used this device to

determine a variety of semivolatile organics in ambient air (19-29). A battery powered, low volume version of this air sampling system has been developed and evaluated (18). It is lightweight, portable and operates very quietly. It is suited for domiciliary air sampling or use as a personal air monitor and both types of monitoring studies have been reported using the device (30, 31). It is also convenient for outdoor use at remote sites where electrical power is not readily available (19).

4.2 Phase Distribution

Many semivolatile organic compounds have vapor pressures that allow them to exist in the atmosphere either as vapors or in the condensed phase, or both, depending on the ambient conditions at the time of sampling. For many purposes it would be desirable to determine the distribution of semivolatile organics between the gaseous and condensed phase in the atmosphere and there have been attempts to accomplish this by choice of the method of sampling. Unfortunately, no satisfactory method has yet been devised to unequivocally make this determination. It is incorrect to assume that the material collected on a filter in front of a vapor collecting sorbent represents the amount of semivolatile organic in the condensed phase in the atmosphere and that the material collected on the sorbent represents the vapor phase of the semivolatile organic. This assumption is faulty because as air passes through the filter during the sampling process, unknown amounts of the semivolatile organic material transfers from the filter to the sorbent. This corrupts the use of the analysis of individual sampling components as a means to determine the distribution of phases, but does not invalidate the total determination. The phase distribution problem has been discussed by Lewis (1) and field experiments to evaluate it in depth have been reported (32,33).

5.0 Nonvolatile Organic Compounds

Nonvolatile organic compounds, i.e., compounds with vapor pressures less than 10^{-8} kPa, for all practical purposes have negligible concentrations in the vapor phase in the atmosphere. These compounds are bound to solid particles and the usual methods of sampling for atmospheric particles, e.g., filtration, are commonly used to obtain samples of nonvolatile organics. By far the most used sampling system is the previously mentioned High Volume sampler. This sampling device, which has been described in detail (35), is widely used to sample large volumes of air, typically 1600 to 2400 m³ using glass fiber filter as a collection medium. Extraction of the collected particulate matter with a solvent is used to isolate the organic compounds of interest and thin layer chromatography or high performance chromatography used for separation and analysis.

Polynuclear hydrocarbons with more than four fused rings, and their nitrogenous and oxygenated derivatives, are, by far, the predominant members of the nonvolatile category. Benzo[a]pyrene, a potent carcinogen resulting from inefficient combustion, is the most studied nonvolatile organic and its ambient concentrations have been widely determined throughout the world for many years. Benzo[a]pyrene is important because it has been a significant air pollutant in the past but levels of this pollutant have been significantly reduced in recent years.

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